

Tracing redox at depth using apatite?

B. A. KONECKE^{1*}, A. FIEGE¹ AND A. C. SIMON¹

¹University of Michigan., Ann Arbor, MI 48103, USA

(*correspondence: bkonecke@umich.edu)

The redox state (fO_2) of magmatic systems is a key variable that influences crystallization and degassing processes, and determines among other things, ore metal ratios in porphyry ore deposits. Apatite [$Ca_5(PO_4)_3(F, Cl, OH)$] is a ubiquitous, resistant mineral in magmatic systems and can contain up to several thousand ppm of S and Mn [1, 2]. Recently, it was reported that Mn contents in some natural apatites correlate negatively with fO_2 , possibly allowing for Mn-in-apatite to be used as an oxybarometer [2]. Sulphur in apatite is another potential fO_2 proxy, considering that S is thought to be incorporated in apatite as sulphate (S^{6+}) [3] and, therefore, the S content of apatite should decrease with decreasing fO_2 ; i.e. with lower S^{6+}/S^{2-} in the melt. In this study, we are experimentally testing the S-in-apatite and Mn-in-apatite oxybarometers.

Apatite is crystallized from rhyolitic melt at 800°C, 200 MPa, and $fO_2 = \Delta NNO + 1$, by seeding the melt with <2µm diameter apatite crystals. Run durations of 10 days yield homogeneous apatite crystals up to 25µm in diameter. Run products are analysed using EPMA. Nernst-type partition coefficients ($\pm 1\sigma$) are $D_S^{Ap/Melt} = 7.9 \pm 2.3$ and $D_{Mn}^{Ap/Melt} = 8.4 \pm 5.7$. We use anhydrite or pyrrhotite to monitor fS_2 since it has been reported that fS_2 affects $D_S^{Ap/Melt}$ [1]. However, this correlation has never been calibrated experimentally.

Our new data indicate that the equation provided by Parat *et al.* [1] for the correlation between the S content in the melt and the S content in apatite underestimates the $D_S^{Ap/Melt}$ by a factor of ~1.7. We suggest that this may simply be related to the lack of data at lower S contents in the melt (< 130 ppm). More puzzling is that the Mn-in-apatite oxybarometer developed by Miles *et al.* [2], which was calibrated using natural samples exclusively, predicts a fO_2 that is ~2 orders of magnitude more reducing than the intrinsic fO_2 of our experiments. Additional inconsistencies arise when comparing the Miles *et al.* [2] model to the experimental Mn-apatite data from Mathez and Webster [4] at lower fO_2 ($\Delta NNO - 2$ to +0). The observed discrepancies between our data and published studies highlight the critical need for additional experimental data that fully constrain $D_S^{Ap/Melt}$ and $D_{Mn}^{Ap/Melt}$ over a wide range of fO_2 , fS_2 and melt compositions.

[1] Parat *et al.* (2011) *Rev. Mineral. Geochem.* **73**, 285–314.

[2] Miles *et al.* (2014) *Geochim. Cosmochim. Acta* **132**, 101–

119. [3] Paris *et al.* (2001) *Can. Mineral.* **39**, 331–339. [4]

Mathez and Webster (2005) *Geochim. Cosmochim. Acta* **69**, 1275–1286.